

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(11) (A) No. 1037973

(45) ISSUED 780905

(52) CLASS 261-24
C.R. CL.

(51) INT. CL. ² C04B 35/00, 35/10, 35/14

(19) (CA) **CANADIAN PATENT** (12)

(54) CERAMIC REFRACTORY FIBROUS MATERIAL

(70) Johnson, Thomas A. and Long, William G.,
U. S. A.

Granted to The Babcock & Wilcox Company,
U. S. A.

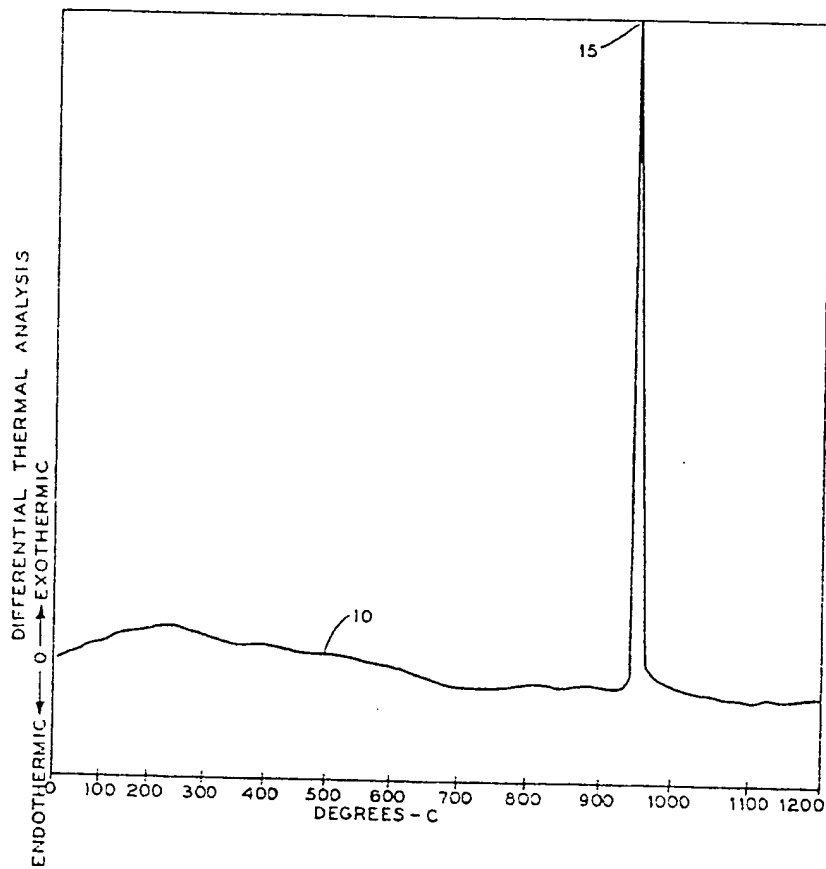
(21) APPLICATION No. 225, 815

(22) FILED 750424

(30) PRIORITY DATE U. S. A. (474, 626) 740530

No. OF CLAIMS 3

FIG. 1



Robert M. Lee

FIG. 2

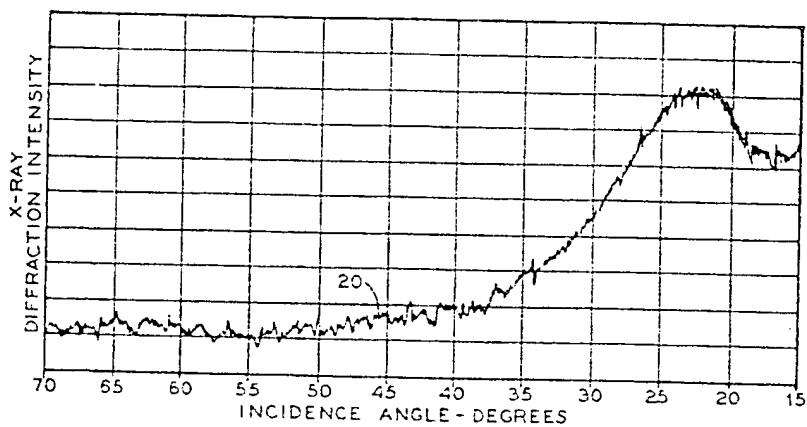
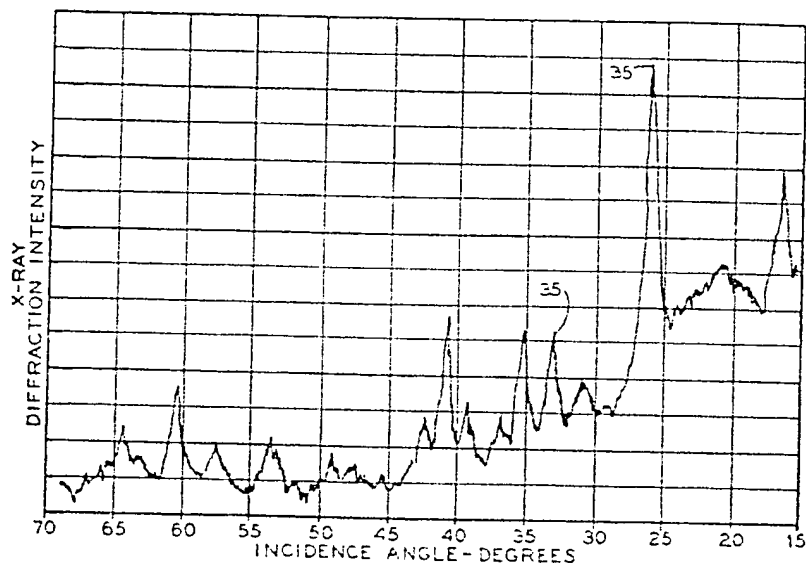


FIG. 3



John Doe

AN IMPROVED CERAMIC REFRACTORY FIBROUS MATERIAL

ABSTRACT

This invention discloses an amorphous ceramic refractory fiber which has been heat treated above its devitrification temperature for a selected period of time to produce a resilient material.

ALL 5/30/74
JMS 5/30/74

This invention relates to ceramic fibrous materials and manufacturing processes for these materials and, more particularly, to an improved ceramic refractory fibrous material of the alumina, silica, and alumina-silica type and techniques for producing these materials.

10 Ceramic fibrous materials have ranged in composition from high purity silica fibers to high purity alumina, with the usual commercial fibers having a general alumina content of from 45% to 77% with a general silica content of 52% to 22%. The commercial fibers will also have extremely small amounts of metallic oxides in the form of contaminants such as iron or the like. Sometimes such small amounts of metallic oxide are deliberately added to attain specific objects in the commercial fibers. Generally speaking, the fibers, as manufactured will contain a major portion of the fibers having diameters in the range of 1 to 10 microns, although submicron and above 10 micron fiber sizes have been produced and used.

20 Ceramic refractory fibrous materials of the alumina, silica, and alumina-silica type have been used for thermal insulation for many years. The usual fiber is commercial manufactured by a jet of air or steam shattering a stream of molten ceramic with the so formed fibers collected in bulk form. Ordinarily, the collected bulk fiber is compressed to form fiber blankets or sheets of a preferred bulk density. These ceramic refractory fibers are glassy or amorphous as manufactured.

30 While the theoretical end use temperature will be at the melting temperature of the ceramic fibers, which will be in excess of 3,000°F, it is known that alumina, silica, and alumina-silica ceramic fibers will be converted from an amorphous form to a crystalline form when heated above the devitrification temperature of the particular composition involved. With the blanket or compressed sheet at typical use temperatures, the fiber will retain a substantially permanent set under compression. When the use temperature is above the devitrification temperature the amorphous fiber will



1037373

be converted to a crystalline form which is subject to degradation due to thermal physical dimension changes or even vibration in the system to which it is applied.

In the interest of material integrity and insulation efficiency, it is clear that a ceramic refractory fiber which resists a permanent set at typical use temperatures is desirable.

In accordance with the invention, a ceramic refractory fiber having a significantly definitive fine-grained crystallinity throughout and, more particularly, an improved stiffness or the
10 improved ability to resist a permanent set than that which heretofore has been available is achieved through a novel heat treatment of the amorphous refractory fibers beyond the devitrification temperature of the material for a selected period of time. Some ceramic fiber material produced through this technique has subsequently shown significantly greater resistance to a permanent set or deformation, at elevated temperatures below the devitrification temperature, than the untreated material. That is, the fiber material returns to 85% to 90% of its original dimension.

The process characterizing the invention is, essentially,
20 a form of heat treatment of the ceramic fiber material in which the material undergoes a change of state from an amorphous or glassy condition to a material having a generally fine grained-crystalline structure. In the course of this heating, the amorphous or glassy state is maintained until a specific temperature of the particular material is reached. At this point, termed the devitrification temperature, the conversion to the crystalline state commences. Because ceramic refractory fibers are significantly known for their insulation qualities, a temperature above the devitrification temperature of the particular material is required to ensure devitrification throughout the material. It is to be noted, however, that excessive temperatures above the devitrification value or sufficiently greater temperature than the devitrification value held for an excessive time tend to produce coarse grained structures with poor handling properties.

1037973

OF THE DRAWINGS:

Fig. 1 is a graph of a Differential Thermal Analysis of a Kaowool* ceramic refractory fiber material;

Fig. 2 is a graph of the X-ray Diffraction Intensity of a ceramic refractory fiber blanket such as shown in Fig. 1 prior to the heat treatment described herein; and

Fig. 3 is a graph of X-ray Diffraction Intensity of the same ceramic refractory fiber blanket of Fig. 2 after heat treatment above the material's devitrification temperature shown in Fig. 1.

10 Fig. 1 graphically illustrates a feature of the invention, that is, the definite nature of the devitrification temperature value for a particular material, by means of a Differential Thermal Analysis of the material. As shown, curve 10 indicates the thermal nature of the tested material with increasing temperature. It is to be noted that at about 950°C or (1,750°F) a definite relatively large and rapid peak 15 in the exothermic regime is indicated. This exothermic peak 15 denotes a change in the state of the fiber material from an amorphous condition to a crystal structure, and the temperature at which this occurs is termed the devitrification temperature.

20 While the specific devitrification temperature shown in Fig. 1 shows a typical curve developed in testing a Kaowool* fiber with a general composition of about 45% alumina and 52% silica, it will be understood the actual devitrification temperature value will be somewhat different for other compositions. However, a definite devitrification temperature value can be found for all alumina, silica, and alumina-silica fibrous materials.

30 Fig. 2 is a graphic representation of the X-ray Diffraction Intensity of the particular ceramic refractory fiber (Kaowool), at various angles of incidence, prior to the heat treatment of the

*Trade Mark

1037973

material above its devitrification temperature, which with the example shown is about 950°C . The relatively smooth nature of curve 20 with respect to curve 30 of Fig. 3 is indicative of the amorphous nature of the fiber material.

Consequently, by heat treating the material of Fig. 2 above its devitrification temperature of about 950°C , the expected crystal formation appears on the X-ray Diffraction Intensity curve as sharp intensity peaks. Fig. 3 depicts the Diffraction Intensity of the Kaowool fiber material of Fig. 2 after heat treating the material to about 950°C - $1,000^{\circ}\text{C}$ for about fifteen minutes. Diffraction Intensity peaks 35 indicate the crystal nature of the once amorphous material.

EXAMPLE:

A ceramic refractory fiber material, such as an alumina-silica fiber refractory, in particular, Kaowool* fiber as sold by The Babcock & Wilcox Company, is heat treated in a muffle furnace. This particular fiber blanket has a density of about eight pounds per cubic foot and a devitrification temperature of about 950°C .

In order to ensure devitrification throughout the entire blanket and to compensate for the cyclic nature of the furnace, that is, the furnace does not hold a set temperature exactly but cycles above and below that temperature, a temperature greater than the devitrification value is preferred. Typically, exposure to a temperature of about $1,000^{\circ}\text{C}$ for about twenty minutes produces the fine grained crystalline structure required to resist a permanent set deformation. X-ray examinations indicate that the average crystalline size in the fine grained alumina-silica fiber is less than 200 angstroms (A).

Although tests indicate that at temperatures up to about $1,050^{\circ}\text{C}$ and for a period of up to thirty minutes does not hinder

*Trade Mark

1037973

the deformation resistance of the material, care must be exercised to limit the heat treatment, especially at temperatures above 1,050°C, in order to prevent excessive grain growth.

Samples of ceramic refractory fiber blanket (Kaowool* fiber) with a devitrification temperature of about 950°C were subjected to average temperatures from about 950°C to about 1,050°C for ten minutes to one hour. These heat treated ceramic fibers, formed as blankets of one inch nominal thickness were then compressed, by a restraining bracket, to 70% of their initial thickness or to 0.7 inches and then exposed to about 815°C for 18 hours. These conditions were imposed to simulate an 18 hour insulation use at the expected temperature and compression in a Gas Cooled Nuclear Reactor. Upon completion of the 18 hour test, the nominal uncompressed material thickness for each of the heat treated ceramic refractory fibrous blankets were as follows:

TABLE I

NOMINAL THICKNESS (INCHES) AFTER 18 HRS @ 815°C

	HEAT TREATMENT TIME MIN.	HEAT TREATMENT TEMP. °C			
		950	980	1,010	1,050
20	10	.72	.96		.82
		.71	.92		.78
	15		.85		.76
			.97		.81
			.80		.81
	25		.89	1.02	1.00
			.84	1.01	.98
			.88	.79	
			1.03		
			.86		
30	30				1.00
					1.00
	60		.83		

Due to the fluffy nature of the fiber blankets, the thickness varies along the dimensions of the blanket and, therefore, is termed a "nominal" thickness.

*Trade Mark

1037973

It will be noted from the above table that it is desirable, under the time schedule indicated, to utilize a temperature of about 30°C to 100°C above the devitrification temperature, of the specific fibrous material treated, to effectively heat treat the material to provide the desired resiliency of the material, which is preferably about 85% to 90% of the original uncompressed fiber thickness.

10 It is well known in the art that ceramic refractory fibrous materials will devitrify when subjected to use conditions exceeding the devitrification temperature. A use temperature significantly above the devitrification temperature will lead to increased crystal growth and defeat the purposes of the invention. Therefore, in accordance with the present invention the improved resiliency of the ceramic fibrous materials attained by the heat treatment prior to use is effective at use temperatures below which the grain growth does not adversely affect the mechanical properties of the fiber.

EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for forming a fine-grained crystalline ceramic refractory fiber material characterized by its ability in use to resiliently return to its original configuration upon application and then release of compression force, which comprises heat treating fibers of a fused glassy ceramic refractory material of preselected density above its devitrification temperature for a period of time long enough to convert the fibers from the glassy condition to a fine-grained crystalline condition and short enough to prevent excessive fiber grain growth.

2. The process of claim 1 wherein heat treating is carried out with an alumina-silica fiber material.

3. A fine-grained crystalline ceramic refractory fiber material characterized by its ability in use to resiliently return to its original configuration upon application and then release of compression force and formed by heat treating fibers of a fused glassy ceramic refractory material of preselected density above its devitrification temperature for a period of time sufficient to convert the fibers from a glassy condition to a fine-grained crystalline condition and yet prevent excessive fiber grain growth.

